Method for the production of hydrocarbon liquids using a Fischer-Tropsch method

The present invention relates to a novel method for converting gaseous hydrocarbons to liquid hydrocarbons using one of the known methods for generating synthesis gas, as well as the Fischer-Tropsch process and in particular, a specific step for treating the waste gas produced by the Fischer-Tropsch process.

It is well known how to convert raw gaseous or solid hydrocarbon compounds to liquid hydrocarbon products usable in the petrochemical industry, in refineries or in the transport sector. Some large natural gas fields are located in remote places and far from any consumer areas; they can accordingly be used by installing so-called "Gas to Liquid (GtL)" conversion plants near these natural gas sources. The conversion of the gases to liquids permits easier transport of the hydrocarbons. This type of GtL conversion is usually carried out by converting raw gaseous or solid hydrocarbon compounds to a synthesis gas mainly comprising H_2 and CO (by partial oxidation using an oxidizing gas and/or reaction with steam or CO_2), followed by the treatment of this synthesis gas by the Fischer-Tropsch process to obtain a product which, after condensation, yields the desired liquid hydrocarbon products. During this condensation, a waste gas is produced. This waste gas contains low molecular weight hydrocarbon products and unreacted gases. In consequence, it is generally used as a fuel in one of the processes of the GtL unit, for example in a gas turbine or a combustion chamber associated with a steam turbine or in an expansion turbine associated with a compressor of the GtL unit. However, the quantity of waste gas to be burned often substantially exceeds the fuel demand of the GtL unit. Moreover, the waste gas also comprises CO_2, which reduces the hydrocarbon product combustion efficiency and which is released into the atmosphere, in violation of environmental standards. Finally, the waste gas generally comprises amounts of unconverted H_2 and CO: hence it is not economical to burn them.

Considering the environmental constraints pertaining to CO_2, it has been proposed to treat the waste gas to strip it of CO_2. US 5 621 155, for example, describes a method in which a portion of the waste gas from the Fischer-Tropsch process is treated in order to remove the carbon dioxide and is then recycled through the step of the Fischer-Tropsch process. However, the remaining portion of waste gas containing H_2 and CO is always burned, and this is uneconomical. Moreover, CO_2 is always released.

WO 01/60773 also describes a method in which the waste gas from the Fischer-Tropsch process is treated to strip it of CO_2. The waste gas with reduced CO_2 content is used as a fuel in various parts of the plant.

US 6,306,917 describes a method in which the carbon dioxide is removed from the waste gas produced by the Fischer-Tropsch process. This patent also describes the treatment of the waste gas to recover the hydrogen using a membrane and the recycling of this hydrogen to the Fischer-Tropsch reactor. The CO compound is sent to combustion.

The object of the present invention is to propose a method for converting gaseous hydrocarbons to liquid hydrocarbons using the Fischer-Tropsch process in which the waste gas from this Fischer-Tropsch process is treated in order to avoid the economic loss of H_2 and CO by simple combustion.

A further object is to propose a method for converting gaseous hydrocarbons to liquid hydrocarbons using the Fischer-Tropsch process in which the waste gas is treated in order both to avoid the economic loss of H_2 and CO by simple combustion and to sharply reduce the atmospheric release of CO_2 by recycling the carbon chains.

The invention has the advantage of adapting to all types of waste gas. Moreover, it allows the re-use, in the GtL process, of the hydrocarbons present in the waste gas. The invention has the major advantage of performing the function of redistributing the various compounds of the waste gas in a plurality of gas streams usable in different steps of the general method for converting gaseous hydrocarbons to liquid hydrocarbons.

For this purpose, the invention relates to a method for converting gaseous hydrocarbons to liquid hydrocarbons in which the Fischer-Tropsch process is employed, said process producing liquid hydrocarbons and a waste gas comprising at least hydrogen, carbon monoxide, carbon dioxide and hydrocarbons with a maximum of 6 carbon atoms, and in which the waste gas is subjected to a separation method producing:

- at least one gas stream comprising methane and for which the recovery rate of hydrogen and carbon monoxide is at least 60%,
- at least one gas stream for which the carbon dioxide recovery rate is at least 40%, and
- at least one supplementary gas stream mainly comprising hydrocarbons with at least 2 carbon atoms.

Other features and advantages of the invention will appear from a reading of the following description. Embodiments of the invention are given by way of non-limiting examples, illustrated by the drawings appended hereto, in which:

- Figures 1 and 2 are flowcharts of a GtL unit incorporating a Fischer-Tropsch process according to the prior art,
- Figure 3 is a flowchart of the method according to the invention.

The invention therefore relates to a method for converting gaseous hydrocarbons to liquid hydrocarbons in which the Fischer-Tropsch process is employed, said process producing liquid hydrocarbons and a waste gas comprising at least hydrogen, carbon monoxide, carbon dioxide and hydrocarbons with a maximum of 6 carbon atoms, and in which the waste gas is subjected to a separation method producing:

- at least one gas stream comprising methane and for which the recovery rate of hydrogen and carbon monoxide is at least 60%,
- at least one gas stream for which the carbon dioxide recovery rate is at least 40%, and
- at least one supplementary gas stream mainly comprising hydrocarbons with at least 2 carbon atoms.

The invention relates to any type of method for converting gaseous hydrocarbons to liquid hydrocarbons using the Fischer-Tropsch process. In general, these gaseous hydrocarbons are produced by a reaction for

producing a hydrocarbon synthesis gas (for example by partial oxidation using an oxidizing gas and steam). This synthesis gas comprises hydrogen and CO. It is normally produced by a unit for preparing a synthesis gas from natural gas or from an associated gas or from coal. According to the method of the invention, this synthesis gas is subjected to a Fischer-Tropsch reaction by contact with a catalyst promoting this reaction.

During the Fischer-Tropsch reaction, the hydrogen and CO are converted to hydrocarbon compounds of variable chain length by the following reaction:

$$CO + (1+m/2n)\, H_2 \rightarrow (1/n)C_nH_m + H_2O$$

CO_2 is also produced during this reaction; for example by the following side reactions:

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$2\, CO \rightarrow CO_2 + C$$

At the exit of the reactor using the Fischer-Tropsch process, the temperature of the products is generally lowered from a temperature of about 130°C to a temperature of about 90 to 60°C, so that, on the one hand, a condensate is obtained, consisting mainly of water and liquid hydrocarbons with more than 4 carbon atoms, and, on the other hand, a waste gas comprising at least hydrogen, carbon monoxide, hydrocarbons with a maximum of 6 carbon atoms, carbon dioxide and generally also nitrogen.

The present invention relates to the treatment of this waste gas obtained. According to the method of the invention, this waste gas is subjected to a separation method producing:

- at least one gas stream comprising methane and for which the recovery rate of hydrogen and carbon monoxide is at least 60%,
- at least one gas stream for which the carbon dioxide recovery rate is at least 40%, and
- at least one supplementary gas stream mainly comprising hydrocarbons with at least 2 carbon atoms. According to the invention, the recovery rate of a compound in one of the gas streams from the separation method corresponds to the volumetric or molar quantity of said

compound present in the waste gas which is separated from said waste gas and which is produced in said gas stream from the separation method with respect to the total volumetric or molar quantity of this compound present in the waste gas. In the case of the gas stream for which the recovery rate of hydrogen and carbon monoxide is at least 60%, the condition of 60% recovery applies both to the CO compound with respect to the quantity of CO initially present in the waste gas and to the H_2 compound with respect to the quantity of H_2 initially present in the waste gas. According to the invention, "gas stream mainly comprising a compound" means a gas stream in which the concentration of this compound is higher than 50% by volume. According to the invention, the separation method used to treat the waste gas is advantageously a pressure swing adsorption (PSA) separation method. This PSA separation method is put into practice using a PSA separation unit used to obtain at least the following three main gas streams:

- at least the first gas stream comprising methane and for which the recovery rate of hydrogen and carbon monoxide is at least 60%,
- at least the second gas stream for which the carbon dioxide recovery rate is at least 40%, and
- at least the third supplementary gas stream mainly comprising hydrocarbons with at least 2 carbon atoms. In general, for the first stream, the carbon monoxide recovery rate is lower than the hydrogen recovery rate (the recovery rate is about 60%-75% for carbon monoxide and about 75%-85% for hydrogen) while the methane recovery rate remains about 55%-65% and the CO_2 recovery rate remains below 1%. The CO_2 recovery rate in the second stream is higher than 40%, preferably higher than 50%. The third stream is a supplementary stream, and can therefore have a CO_2 recovery rate of at most 60%, preferably at most 50%. The second gas stream can comprise methane.

The separation method can also be used to produce at least one gas stream mainly comprising hydrogen. According to a first variant of the method according to the invention, the same PSA separation unit of the separation method used to treat the waste gas can also be used to

produce at least one gas stream mainly comprising hydrogen. This stream can have a hydrogen concentration above 98% by volume. According to an alternative to this first variant of the method according to the invention, the separation method used to treat the waste gas can put into practice a second PSA separation unit intended to produce at least one gas stream mainly comprising hydrogen. This stream can have a hydrogen concentration above 98% by volume.

The waste gas can also comprise at least nitrogen and the waste gas separation method can produce at least one gas stream comprising at least nitrogen. In general, this gas stream comprising nitrogen corresponds to the gas stream mainly comprising hydrocarbons with at least 2 carbon atoms.

Preferably, each adsorber of the PSA separation unit is composed of at least three adsorbent beds:

- the first bed being composed of alumina,
- the second bed being composed of a silica gel, and
- the third bed being composed of at least one adsorbent selected from either zeolites or carbon molecular sieves, with average pore sizes between 3.4 and 5 Å and preferably between 3.7 and 4.4 Å, or a titanium-silicate with average pore sizes between 3.4 and 5 Å, and preferably between 3.7 and 4.4 Å.

Depending on the different pressure cycles, the PSA separation method can be used to obtain in succession:

- a high pressure gas stream comprising methane and for which the recovery rate of hydrogen and carbon monoxide is at least 60%, and
- a gas stream for which the carbon dioxide recovery rate is at least 40%, and then
- a supplementary gas stream mainly comprising hydrocarbons with at least 2 carbon atoms.

Alumina can be used to remove the water present in the waste gas and the hydrocarbon compounds with 5 or more carbon atoms. Silica gel can be used to adsorb the hydrocarbon compounds and particularly the hydrocarbon compounds with at least 3 carbon atoms. Preferably, the silica gel used has an alumina (Al_2O_3) content of less than 1% by weight.

On the contrary, alumina and silica gel allow any H_2, CO and CH_4, and CO_2 and N_2 present in the waste gas to pass through. Zeolites or carbon molecular sieves with pore sizes as previously defined can be used to adsorb the carbon dioxide, and also partially the nitrogen. The choice of a titanium-silicate instead of the third zeolite bed or carbon molecular sieve bed also serves to retain the CO_2. The order of the three adsorbent beds is preferably the following, in the waste gas flow direction in the adsorber: first bed, then second bed, then third bed.

According to the first variant of the invention, each adsorber of the PSA separation unit can also comprise a fourth adsorbent bed in the waste gas flow direction in the adsorber; this fourth bed can be a zeolite or an activated charcoal if the third bed is a carbon molecular sieve. If the alternative to the first variant of the method according to the invention is put into practice, the adsorber of the second PSA separation unit producing at least one gas stream relatively pure in hydrogen (hydrogen concentration above 98% by volume) is composed of an adsorbent bed comprising at least one activated charcoal. In this case, at least a portion of the first stream from the first adsorption unit is introduced into this second adsorption unit.

Each adsorber of the PSA separation unit can also comprise a fourth or fifth bed comprising at least one titanium-silicate or one zeolite; this makes it possible to stop the nitrogen, at least partially. Preferably the titanium-silicate and zeolite have an average pore size of about 3.7 Å, or preferably between 3.5 Å and 3.9 Å; they are preferably exchanged with lithium, sodium, potassium or calcium, or are a combination of these elements. The structure of the zeolite is preferably selected from the following structures: LTA, CHA, AFT, AEI-AlPO18, KFI, AWW, SAS, PAU, RHO.

According to a first embodiment, downstream of the waste gas treatment, the gas stream from the separation method, comprising methane and for which the recovery rate of hydrogen and carbon monoxide is at least 60%, can be treated by a cryogenic unit in order to produce:
either, according to a first version:

- at least one stream essentially comprising hydrogen and carbon monoxide, and
- at least one stream mainly comprising methane,

or, according to a second version:

- at least one stream essentially comprising hydrogen,
- at least one stream mainly comprising carbon monoxide, and
- at least one stream essentially comprising methane.

"Stream essentially comprising" a compound means a stream comprising at least 85% by volume of the compound, and preferably at least 95%. Thus, according to the first version, after decarbonation, and cooling of the gas stream comprising methane and for which the recovery rate of hydrogen and carbon monoxide is at least 60%, it is possible to use a column for separating the liquid phases condensed from the vapor phase, the vapor phase essentially consisting of hydrogen and CO, while the condensed phase mainly consists of methane. According to the second version, after decarbonation and cooling of the gas stream comprising methane to at least minus 150°C, for which the recovery rate of hydrogen and carbon monoxide is at least 60%, it is possible to use a methane scrubbing column to absorb the CO and to produce: at the top of the column in the vapor phase, a stream essentially comprising hydrogen, and at the bottom of the column, a condensed phase essentially containing methane and CO, which is sent to a CO/hydrocarbon distillation column to generate: at the top, a stream mainly comprising CO, and at the bottom, a stream essentially comprising methane.

According to a second embodiment, downstream of the waste gas treatment, the gas stream from the separation method, comprising methane and for which the recovery rate of hydrogen and carbon monoxide is at least 60%, can also be treated by a downstream PSA method in order to produce:

- at least one stream essentially comprising hydrogen, and
- at least one stream mainly comprising carbon monoxide and methane.

The various gases from the waste gas separation method can then be utilized in various parts of the GtL unit. Thus, at least a portion of the gas stream from the waste gas separation method, comprising methane and for

which the recovery rate of hydrogen and carbon monoxide is at least 60%, can be used as reagent gas in a unit for preparing a synthesis gas comprising H_2 and CO, if any, and/or as reagent gas in the Fischer-Tropsch process. Similarly, at least a portion of the gas stream from the waste gas separation method, mainly comprising hydrocarbons with at least 2 carbon atoms, can be used as fuel and/or as reagent gas in the generation of synthesis gas. At least a portion of the gas stream from the waste gas separation method, mainly comprising hydrogen, can be used for hydrocracking processes, like the one used to treat liquid hydrocarbons with more than 4 carbon atoms and produced by the Fischer-Tropsch process. Finally, at least a portion of the gas stream from the waste gas separation method, for which the carbon dioxide recovery rate is at least 40%, can be used as reagent gas in a unit for preparing a synthesis gas comprising H_2 and CO, if any, or as reagent gas in the Fischer-Tropsch process. The latter case is useful when the Fischer-Tropsch catalyst produces CO_2 from CO; the reaction can then be equilibrated and the overproduction of CO_2 avoided. The removal of the methane from certain streams serves to prevent its accumulation during the recycling of these streams, particularly in the stream that is recycled to the Fischer-Tropsch process.

Figure 1 shows a method of the prior art in a GtL type of plant. A raw gas (1) is treated in a unit for preparing a synthesis gas (A) to supply a synthesis gas (2) containing hydrogen and CO. This synthesis gas (2) is sent to a Fischer-Tropsch unit (B) where it is subjected to a Fischer-Tropsch reaction followed by condensation, for example in a settling drum. The products from the Fischer-Tropsch unit are:

- the condensate (3) from condensation which mainly comprises water. This condensate is removed from the GtL plant.
- liquid hydrocarbon compounds (4) with more than 4 carbon atoms. These compounds are generally subjected to a treatment (C) for cutting their long chains and for obtaining chain lengths of at least 6 carbon atoms, for example, using hydrogen. The hydrocarbon compounds with a smaller number of carbon atoms (8) are used as fuel in an electricity generating unit (D).

- a waste gas (5) comprising a mixture of H_2, CO, CO_2 and light hydrocarbons with a maximum of 6 carbon atoms, which can be either partially (6) reintroduced into the Fischer-Tropsch reactor, or partially (7) used as fuel in an electricity generating unit (D) or a steam production unit.

Figure 2 shows the method put into practice in Figure 1, but in which the waste gas (5) is treated by a CO_2 stripping unit (E). The CO_2 recovered in (9) is injected into the synthesis gas production unit (A).

Figure 3 shows the method according to the invention. Unlike the methods of the prior art shown in Figures 1 and 2, the waste gas (5) comprising a mixture of H_2, CO, CO_2 and light hydrocarbons with a maximum of 6 carbon atoms, is treated at least partially (10) by a separation method (F) yielding:

- a gas (11) mainly comprising hydrocarbons with at least 2 carbon atoms, which can partially (11a) be recycled to synthesis gas generation (A), or partially (11b) used as fuel in an electricity generating unit (D),
- a gas (12) mainly comprising hydrogen. This gas (12) can be used during the treatment (C) to cut the chains of the liquid hydrocarbon compounds (4) from the Fischer-Tropsch process,
- a gas (13) comprising hydrogen and carbon monoxide with a recovery rate of at least 60% and methane, which is recycled to the Fischer-Tropsch reactor (B), and
- a gas (14) comprising CO_2 with a carbon dioxide recovery rate of at least 40%, which is introduced into the synthesis gas preparation unit (A)